Analytical Methods

Radiochemistry

Paragon Analytics SOPs:

SOP 713 REV 8
SOP 739 REV 8
SOP 704 REV 7
SOP 726 REV 4

PARAGON ANALYTICS, INC.
STANDARD OPERATING PROCEDURE 713 REVISION 8

TITLE: ANALYSIS OF GAMMA EMITTING RADIONUCLIDES BY GAMMA SPECTROSCOPY – METHOD EPA 901.1

FORMS None

APPROVAL:
Technical Manager _____ Date 4/6/03
Quality Assurance Manager _____ Date 04.04.03
Laboratory Manager _____ Date 4-6-03

HISTORY: Rev 0, 06/01/92; Rev 1, 07/27/93; Rev 2, 10/15/93; Rev 3, 04/26/96, Rev 4, 05/16/96, Rev 5, 03/20/00; Rev 6, 06/15/01; Rev 7, 08/24/02; Rev 8, 04/07/03. *dbh*

1. SUMMARY, SCOPE AND APPLICATION

1.1 SUMMARY

Gamma emissions from radionuclides are detected by a semiconductor germanium crystal, which provides a small electronic pulse for each gamma interaction, where the pulse height is proportional to the gamma incident energy. This electronic data is converted to digital data by an analog to digital converter (ADC) and stored in a multichannel analyzer (MCA). The data collected by the MCA is subsequently interpreted by a complex software program, generating results in units of radioactivity per unit sample volume. The analysis software used by PAI is Seeker®, Gamma Spectroscopy Software, Version 2.2., a product of Vertechs Software Solution, Inc.. This procedure is a more detailed variant of EPA Procedure 901.1 and DOE/EML Procedure 4.5.2.3, and incorporates all of the intentions of EPA 901.1 and DOE 4.5.2.3.

1.2 SCOPE AND APPLICATION

This procedure describes the steps necessary to perform gamma emissions analysis of samples of various media using high-resolution intrinsic germanium gamma spectrometry. This procedure is applicable to all gamma spectrometry analyses performed at Paragon.

2. DISCUSSION/COMMENTS

The physical shape of the source and its proximity to the detector is critical to the efficiency calibration and these factors define the "counting geometry". The calibration geometry and the sample geometry must match within +/- 0.5cm of the line on the sample container.

3. REAGENTS AND APPARATUS

3.1. REAGENTS

No reagents are used by this procedure. The operator should be aware, however, that

water samples are preserved to pH <2 with HNO_3.

3.2. APPARATUS

This procedure is conducted with the use of installed gamma detection and analysis equipment consisting of ten intrinsic germanium gamma spectrometers mounted in lead shields for the reduction of ambient background radiation, a personal computer analysis system with multichannel analyzer interfaces, three NIM-bin based multichannel analyzers, gamma analysis software, and associated nuclear electronics and cabling.

4. PROCEDURE

4.1. OPERATING CONDITIONS

The gamma spectrometry systems shall be operating with detector bias as specified by the detector manufacturer and amplifier and MCA settings as required to obtain a nominal 0.5 keV/channel energy calibration across a range of 47.5 to 2000 keV. The operating conditions shall be verified daily by performance of the daily quality control checks (see Section 5.1).

4.2. PROCEDURE

4.2.1. Spectrum Acquisition

The detector must be calibrated for the geometry that is being loaded. Efficiency calibration procedures are defined in Section 5.2. A list of current geometries, calibration date and the dates the calibrations expire, and standards used for calibration is attached to the top of each detector. Samples shall be placed directly on the detector, inside the lead shield, and should be level and centered over the detector.

After samples have been loaded in the detectors, select the desired detector in the spectral display control menu. After the detector has been selected, select the 'TOOLS' icon. The next prompt will ask for the ID and the desired live time or count time. Enter the sample ID as it appears on the benchsheet followed by a space and then the batch ID (i.e. 0011222-3 GS09999). After the ID has been entered, select the 'ID SET' icon to save the sample ID. Enter the desired count time in seconds in the box labeled 'LIVE TIME' and then select the 'PRE SET' icon to save the count time. Sample count times depend on the sample volume, geometry, and the client's required MDC. An outline of the geometries and their respective matrix and/or volume can be found in Appendix C. The LCS samples are typically counted for 1800 seconds (30 minutes) and blank samples will be counted for as long as the longest sample count time. After the sample ID and count time have been entered and saved, clear the previous spectrum by selecting the erase icon. Begin spectrum acquisition by selecting the 'GO' icon and exit the 'TOOLS' window by selecting 'DONE'.

Enter all samples that are analyzed in the Gamma Spectroscopy Logbook, on the

current page with the date that the sample is being counted. Ensure that the detectors being used have passed the Daily QC checks. Necessary information includes: the PAI sample ID , the detector number, the geometry, the duration of the count, the count start time, and the operators initials. Additionally, for counting geometries 7 and 8 a puck must be used. A run log notation should be entered denoting that the puck was used for these geometries.

4.2.2. Spectrum Analysis

Upon completion of the sample count the data must be transferred to the workspace and analyzed . First select the appropriate analysis/application type in the application select on the menu bar. Then select <Read MCA> on the menu bar. By "reading the MCA", the data acquired during the analysis count is transferred to the workspace and default settings and files from the application are applied. (i.e., efficiency, library, units, etc.) When "Read MCA" is selected the spectrum parameters screen is prompted. At this time the file name is generated and should be recorded in the gamma spec. run log. The analyst will need to enter some parameters and also has the opportunity to change existing parameters for a particular analysis.

Sample ID: This should be automatically transferred, but corrections can be made here.

Spec. Code: This is entered the same as the file ID, except ends in a given letter instead of .SPC. For example if the file ID is 001111.SPC, the Spec. Code would be 001111A. This code is used to store the spectral data in the database file and later transfer the data to Radchem for reporting. The letter is used to designate multiple analyses of the same spectra (ie. 001111A for the first analysis and 001111D for the fourth analysis).

Sample Size: Enter the volume, weight, or number of filters as appropriate.

Units: This will be transferred automatically as a default, but can be changed as needed.

Sampling Start and Stop: Enter the collection date of the sample in both boxes. This is normally the same date and time for both the start and stop. The time of day is generally 12:00:00 for all samples.

Efficiency File: This line should be generated automatically by the computer and is in the form (Dxx)(ShGG).EFF where xx is the detector number, and GG is the geometry of the sample. If changing the efficiency file, make sure the detector of the efficiency file is for the detector the sample was counted on and that the efficiency file has not expired.

After all the parameters and values are satisfactory, select 'OK' to exit the 'Read MCA' window. By selecting 'OK', all of the parameters and values are saved under the file ID and can be retrieved later to further analyze. By selecting

'CANCEL', all of the parameters are lost and the file ID is not saved.

Next, the spectrum must be analyzed to identify peaks at the various energies. To do this, select 'PEAK SEARCH' on the menu bar and the software will apply the resolution calibration to the acquired spectrum to define peaks and peak height. This will prompt the next window, which allows the analyst to see all of the peaks identified, and the counts acquired for each peak. The analyst shall review the peak search results to identify peak shifts, multiplets, etc. After the peak search results are considered to be satisfactory, select 'DONE' to exit the peak search results window.

To calculate activity concentrations, select the 'Calculate' icon under 'Activity' on the menu tool bar. This will prompt an activity report parameters window. Select the desired library to be used in the column labeled 'Library File'. Next select the background file to be used according to the detector and the count date. Background files are named so that the first two numbers correlate to the detector, the next two correlate to the month the background counted, and the next two correlate to the day of the month. Background files can be used for one week after counting. The LSF File should remain as 'NONE'. The 'Results File' and the 'Printout File' should be the same as the .SPC file, except ending in .RSF and .TXT, respectively.

Select 'OK' after the correct library and background have been selected and the library search results window will be shown. This allows the analyst to review peaks that have been matched to specific peaks in the library.

To finish the calculations, select 'OK' to prompt the raw data printout. This window allows the analyst to review all of the parameters used in the analysis. To save the data select 'Database' to prompt the results export parameters window. Here the Spec. Code is used to transfer the raw data to a database later used for reporting. Select 'GAMMA.SDF: Example' in the Export Defs File column and then select 'OK' to transfer the data. Then print the raw data by selecting the printer icon.

5. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

5.1. QC MONITORING

Quality Assurance and Quality Control practices will be performed in accordance with the procedures set forth in PAI's Environmental Radiochemistry Quality Assurance Plan. Standards for Daily QC Checks shall be traceable to the National Institute for Standards and Technology (NIST). All Daily QC monitoring should be recorded in the gamma spectroscopy run log.

5.1.1. Daily QC Energy Calibration Checks

A daily QC check involves performing an energy calibration (as well as monitoring the resolution and efficiency calibrations). Each detector has a labeled calibration

standard. Center the appropriate calibration standard on the corresponding detector. Count each Daily Check standard as described above for 20 minutes using the sample ID "DAILY CHECK". When the count is complete select 'Daily Performance Check' under the Application Select menu and then select 'Read MCA' and the edit parameters screen is then prompted. Select 'OK', as the parameters should be the default.. On the menu bar select <PEAk Search> as described above and then select <Q.C.> on the menu bar and then <Detector> . The calibration parameters screen is then prompted and the energy bullet should be selected. Select <OK>. Choose <Merge PSR> , then select <Curve Fit> and then select <Save>. This will save the energy calibration for that day The program then compares the results of the energy recalibration to the Q.C. parameters (found in the Q.C. editor) established for the specified detector.

5.1.2. Corrective Action for Daily QC failures

If a detector is not within established control limits for any of the bounds tests corrective action must be taken. The first course of action is to re-run the QC check. If the observed parameter is still outside normal acceptance criteria after the second analysis, the procedure is as follows:

5.1.2.1. Daily Energy Calibrations

If one of the centroids exceeds the bounds test (i.e. 662 keV), the peak location should be adjusted. This is done by placing a calibration source on the detector (preferably a Laboratory Control Sample--LCS) and starting the detector Clear the current spectrum by typing <F4> (Clear). The acquisition can then be started by typing <F2> . Move the cursor to the appropriate centroid (i.e. 662 keV) and check the actual location. The peak can be moved by adjusting the fine gain, located on the amplifier. Note that it only requires a minute adjustment (one click) to move the peak three to five keV.

After the peak has been moved to the correct location, re-run the energy calibration.

If the failure includes one of the other parameters (i.e. FWHM or efficiency), the Daily QC can be re-run (if the QC fails for a second time the detector is taken off-line and the lab supervisor should be contacted). Note: A gain adjustment or/and a pole-zero adjustment can be conducted in the case of a FWHM failure. 1. Attach a co-axial cable from the "1 Meg" port associated with the vertical input on the oscilloscope to the "uni" output on the amplifier. 2. The scope settings should be as follows:

Volts/Div(Vertical)= 0.1
Polarity= DC
Trigger Selector= EXT(-)
Mode= DC
Triggering Level=0
Stability= Preset
Time/Div= 20μs

Variable= Calibrated
3.Place a source on the detector and adjust the signal so that it is as close to the baseline as possible by using the "PZ ADJ" dial found on the amplifier.
The energy calibration can now be run again. If any parameter still fails, tag the detector out of service and notify the lab supervisor.

NOTE: Record all calibration operations in the run log, including fine gain adjustments, bounds re-calculations with start and end dates, and calibration re-runs.

5.2. EFFICIENCY CALIBRATION PROCEDURES

Standards for calibration shall be traceable to the National Institute for Standards and Technology (NIST). Standards will normally be of the mixed-gamma, multiple-energy type available from several commercial suppliers. The analysis systems shall be calibrated for each physical form of sample to be analyzed (e.g., water, soil, filter, etc.) at least annually. A FWHM calibration should also be performed at least annually. Note that there is only one FWHM calibration per detector, and it is not geometry specific. Before starting an efficiency calibration, consult with a Senior Instrument Technician. All efficiency calibrations should be recorded in the gamma spectroscopy run log.

5.2.1. Spectrum Acquisition

Place the calibration source for the appropriate geometry on the detector to be calibrated. The efficiency calibration will be initiated like that of a sample count. First, an internal workorder number must be obtained from the current non-client workorder notebook (located in the radium/strontium lab). Use this workorder number and follow the same procedure used to count a sample. Be sure to enter the appropriate dates and time for the calibration standard. (2 hours and/or a duration long enough to acquire 10,000 cts/per energy line that will be used in the calibration.

5.2.2. Spectrum Analysis

5.2.2.1. After the acquisition is complete the MCA of the sample spectrum should be read. In the edit parameters screen enter the standard calibration origin date, and the appropriate volume/sample size. Select <Pk Search> and then select <Calibrate>. The types of calibrations given are: Energy, FWHM, and Efficiency, select <Efficiency>. The calibration parameters screen is prompted, at which time the operator must choose the appropriate calibration standard, aliquot size and the appropriate fit formula for the efficiency curve (exponential fit is used in most cases). Select <OK>, at which time the calibration workspace is prompted. Transfer the peak search results by selecting <Merge PSR> , then select <Curve fit>. View the results of the calibration. The % difference for the measured efficiency should be less than +/- 5 for all nuclides, but may be up to 10% with specific written approval

from the instrument lab supervisor . If the measured difference exceeds this criteria5 the calibration will have to be redone. If efficiency limits are met select <OK> , <Save>, and then print the calibration printout. This calibration should be done annually or when extensive maintenance has been conducted on the detector.

5.2.2.2. If the observed efficiencies need to be adjusted to optimize the fit of the calibration curve this may be done with the approval of the lab supervisor. DO NOT ADJUST THE CS-137 EFFICIENCY. If the other efficiencies need to be adjusted, manually calculate the new efficiency, by either increasing or decreasing by a known percentage (usually 5 to 10%). After adjusting a peak re-start the calibration process (choose the print to screen option until the efficiencies have been accurately adjusted). Manual adjustments are conducted in the calibration work space.
NOTE: DO NOT MANUALLY ADJUST EFFICIENCIES WITHOUT FIRST CONFERRING WITH A SENIOR INSTRUMENT TECHNICIAN.
In all cases, manual adjustments of peak efficiencies will be noted on the calibration output page.

5.2.2.3. After the calibration has been stored, analyze an LCS with the appropriate geometry for 1800 sec to verify the calibration. This analysis must pass normal LCS acceptance criteria.

5.3. Weekly Background Calibration

5.3.1 A background calibration is performed weekly. If this is the first weekly calibration of the month check out an internal work order number from the logbook located in the preparation laboratory. If you are running the second set of calibrations since the beginning of the month, add 10, etc. to the sample number. Assume that one set of calibrations has been run since the beginning of the month, and the second calibration is about to be started. The counts would be named, for example, 9813001-11 for detector 1, 9813001-12 for detector 2, and so on.

5.3.2 Make sure there is no sample in the detector shield. Consult the Gamma Spec Maintenance Logbook to see if the detectors have been cleaned within the past month, if not the detectors need to be cleaned as described in Section 5.3.5.

5.3.3 Start the counts for 1000 minutes (60000 seconds) for each detector in service. Geometry and aliquot are irrelevant.

5.3.4 Record detectors that have been started in the logbook. After the count is complete, read the MCA and do a peak search as described above. In the peak search results save the background calibration by selecting 'Save As BkgSub'. Save each background file as DET##MMDD.BKG, where '##' is the detector number and

'MM' and 'DD' is the month and day the background was started. Then select 'Background' under 'QC' on the menu bar. Select 'OK' to analyze the background and see if the count is within control limits. Record any failures in the run log , clean the detector, and restart the background calibrations.

5.3.5 Weekly Calibration Failures

The inside of the detector must be thoroughly cleaned with a paper towel dampened with Radiacwash®, or an equivalent EDTA solution. Then wipe the detector with a paper towel dampened with DI water. Record the cleaning date in the Gamma Spec Maintenance Logbook.

After this has been done, the background calibration can be run again. If the detector fails after cleaning, the lab supervisor must be notified and the detector must be tagged out of service until the problem is resolved.

5.4 QC Samples

One LCS and blank, per geometry, should be analyzed with every 20 samples. A set of shared QC samples can be used for multiple work orders.

6. INTERPRETATION OF DATA

6.1.RESULTS INTERPRETATION

The spectrum analysis capabilities of the analytical software are only as good as the software set up. It is essential that appropriate analysis geometries, efficiency files, and library file be used to ensure accurate analyses. Results data must be reviewed as soon as it becomes available to ensure that the efficiency file used was appropriate to the sample volume and container design, to ensure that all peaks in the spectrum were matched to a radionuclide, and that, where applicable, the presence of a given radionuclide is supported by the presence of other significant gamma emissions from that radionuclide. All unknown peaks greater than 5 times the listed critical level must be qualitatively identified in the case narrative. In some cases, at the supervisor's or client's request, these radionuclide concentrations may need to be quantified..

The spectrum must also be reviewed to ensure that characteristic peaks, such as K-40 at 1460 keV, and the annihilation peak at 511 keV, do not show evidence of a gain shift. A gain shift would show up as a secondary peak slightly offset from all the normal characteristic peaks in the spectrum. A spectrum that shows evidence of a gain shift must be rejected and the sample re-counted. The detector showing the gain shift must have the fine gain on the amplifier adjusted as described above.

7. PERIODIC MAINTENANCE

7.1. LIQUID NITROGEN

Each detector has a Dewar filled with liquid nitrogen to keep the germanium detector cold. Twice per week, the detector Dewar must be filled with liquid nitrogen. Allow 15 minutes after filling before resuming data acquisition.

If a Dewar runs out of liquid nitrogen between fillings, the red bias display, located on

the "BIAS SUPPLY" control board, will be shutdown. If this occurs, tag the detector out of service, and do not operate the detector until the Dewar can be re-filled. The detector may need to be cycled through ambient room temperature before being re-cooled. The lab supervisor must be notified before proceeding.

7.1.1 Filling the Dewar

After the nitrogen lines have been attached to the "LIQUID" output of the new tank, flip the "SOLENOID CONTROL" switches to the "ON" position. This switch is located on the "AUTO FILL EXPANSION CONTROL" board. Then depress the red "Manual" fill button on the "AUTO FILL CONTROLLER". Once the Dewars have been filled, the red LED read-out on the "AUTO FILL CONTROLLER" should read "168.0", which indicates the number of hours until the next fill should be done.

If a tank has not been completely filled, an alarm will sound. To silence the alarm, depress the "ALARM RESET" button on the "AUTO FILL CONTROLLER". Once the alarm is shut off, check the "AUTO FILL EXPANSION CONTROL" board to see which detector LED lights are on (note that the "SOLENOID CONTROL" switch will still be in the "ON" position if a Dewar has not been completely filled).

To re-fill a partially filled Dewar, the nitrogen lines must be allowed to defrost for about 4 hours. After the lines have defrosted, depress the two red "ERROR RESET" buttons on the "AUTO FILL EXPANSION CONTROL" board and then depress the "MANUAL" fill button.

Each detector is equipped with an overflow line. If this line appears to be bleeding an excessive amount of liquid nitrogen, the "SOLENOID CONTROL" switch should be turned to the "OFF" position.

Record all liquid nitrogen fills and re-fills in the "Gamma LN2 Fill" logbook.

8. DEVIATIONS FROM THE METHOD

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ± 20%, irrespective of the lab's internally derived acceptance criteria.

9. SAFETY, HAZARDS, AND WASTE DISPOSAL

9.1. SAFETY

Normal laboratory safety procedures (gloves, safety glasses, and lab coats, where necessary) must be complied with during the conduct of this procedure. No special safety requirements are mandated by this procedure.

9.2. HAZARDS

9.2.1 Bias applied to detectors is typically in the range of 1000 to 4000 volts DC. This can result in electric shock if bias cables are disconnected while bias is applied.

To minimize the possibility of electric shock, bias will be turned off to any detector before any cabling is disconnected.

9.2.2 The liquid nitrogen used to fill the Dewars is at -196°C. Exposure to the skin can cause severe frostbite. Use insulated gloves when handling frozen lines, valves, etc.

9.2.3 Large spills can displace room oxygen and cause asphyxiation. In case of a large spill, open the lab doors and allow the liquid nitrogen to dissipate before re-entering the lab.

9.3. WASTE DISPOSAL

The gamma spec instrument technician is responsible for returning the samples to the sample custodian or to the sample storage area after analysis, completing the internal chain of custody paperwork.

Some samples will be returned to the client after analysis. Samples or sample wastes containing radioactive materials, which are not being returned to the client, must be disposed of according to PAI's procedures for disposal of radioactive materials. Contact the site WDC for more information.

10. REFERENCES

10.1. Lloyd A. Currie, "Limits for Qualitative Detection and Quantitative Determination," Anal. Chem. 40, 586-93, March 1968.

10.2 ANSI N42.14, American National Standards Institute, Calibration and Usage of Germanium Detectors for Measurement of Gamma Ray Emission of Radionuclides, April 1978, Reaffirmed April 1985.

10.3 EPA-600/4-80-032, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Method 901.1, Gamma Emitting Radionuclides, August 1980.

APPENDIX A
MINIMUM DETECTABLE ACTIVITY CALCULATION

The equation below is taken from "The Minimum Detectable Activity Concept"[1], and implemented by Paragon's gamma analysis software.

$MDA = K * (2.71 + 3.29 * S_b)$,

where $K = 1/(VATCE\ e^{(-\lambda t)})$;

A = the fractional abundance of the radiation emission;

V = the sample volume;

T = the counting time for the background count;

C = the conversion from count rate to activity units;

E = the fractional counting efficiency;

$e^{(-\lambda t)}$ = the decay correction from sampling to counting;

S_b = the standard deviation of the background counts.

APPENDIX B
COMMON GAMMA ENERGIES AND CHANNEL LOCATIONS

This section is provided to assist in determining proper channel locations during calibrations and QC checks.

NUCLIDE	ENERGY (keV)	TARGET CHANNEL
Am-241	59	120
Cd-109	88.04	176
Co-57	122.06	244
Cs-137	661.65	1324
Y-88	898.04	1796
Co-60	1173.22	2346
Co-60	1332.49	2664
Y-88	1836.06	3672

NOTE: Paragon uses a 2.0 keV matching tolerance for nuclide/energy matching; this will allow up to a 4 channel deviation from target channels. In addition, the QC checks perform energy versus channel calibrations each time they are run (normally daily), correcting for small changes in peak channel locations.

APPENDIX C
GEOMETRY/EFFICIENCY LIST

Geometry number	Geometry Description	Default count time (min.)	Efficiency file number	Standard file number
01	1 liter H_2O in 2 liter Marinelli	300	01	01
02	3.5 liter H_2O in 4 liter Marinelli	300	02	02
07	47 mm Filter	60	07	07
13	500 g Solid	30	13	13
11	100 g Solid	30	11	11
17	215 g Solid	30	17	17
26	215 g Solid (Ra-226)	30	26	26

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APPENDIX D. SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency Check	Daily	Within derived control limits.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Peak Resolution Check	Daily	Within derived control limits.	Recount, re-evaluate, perform pole-zero adjustment, if necessary, and repeat daily performance checks.
Energy Calibration	Daily	Within derived control limits.	Recount, re-evaluate, perform fine gain adjustment, if necessary, and repeat daily performance checks.
Peak Background Calibration	Weekly	Within derived control limits	Clean detector, recount, re-evaluate, or document why condition is acceptable.
Efficiency Calibration	Yearly, for each counting geometry.	Each fitted value is within 5% of the observed value. Subsequent LCSs pass within normal acceptance criteria.	Tag geometry off-line. Determine and correct problem; verify source activity; recount and/or recalibrate. With supervisors written approval, fitted values may be within 10% of observed value.
Peak Resolution (FWHM) Calibration	Yearly	Each fitted value is within 10% of the observed value. Subsequent LCSs pass within normal acceptance criteria.	Perform pole-zero adjustment, if necessary, and repeat.
Gain shift	Each sample	Review each spectrum to ensure that characteristic peaks @ 511, 1460 KeV are present, not shifted during the count, and properly ID'd by software.	Recount sample after daily performance checks are successfully performed.

Note: This SOP and SOP 715 contain acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 739 REVISION 8

TITLE: **PREPARATION OF SAMPLES FOR ANALYSIS BY GAMMA SPECTROSCOPY**

FORMS: **302**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 1/31/05

QUALITY ASSURANCE MANAGER _____ DATE 1/31/05

LABORATORY MANAGER _____ DATE 1/31/05

HISTORY: Rev0, 9/20/93; Rev1, PCN #104, 1/24/94; Rev2, PCN #412, 3/21/95; Rev4, 10/12/00; Rev5, 3/11/02; Rev6, 4/07/03; Rev7, 8/27/03; Rev8, 10/3/03 and 1/31/05 (no revisions).

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps used to prepare soil, water and sludge samples for gamma spectroscopy analysis. Vegetation, air filter and bioassay samples are not addressed in this SOP, and must be handled on a case-by-case basis.

2. SUMMARY

Soils and sludges are prepared (i.e., dried and sieved) per SOP 721, prior to beginning the procedure outlined in this SOP. Some soils and sludges may omit such preparations if approval is given by the Radiochemistry Manager or Project Manager. Waters are either filtered or left unfiltered prior to preparation as per work order or Radiochemistry Manager instructions. Waters are measured volumetrically into an appropriately sized Marinelli beaker. Soils are measured gravimetrically into a Lerner jar or an aluminum can, as appropriate for the sample size and the analyte. The gamma spec containers are sealed with their lids, and wiped with a damp paper towel to remove potential contamination.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 These procedures are to be performed only by personnel who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must

be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Gamma spec samples must be produced only in the specific geometry for which the Instrumentation Group has calibrated their spectrometers.

4.2 New containers ordered for gamma spec must be equivalent to those currently in use. The Instrumentation Laboratory Supervisor must approve the use of alternate containers or supplies in advance.

4.3 Gamma spec containers are not reusable due to the possibility of carry-over in the next analysis. Once the analysis is complete, the container is returned to the sample storage area.

4.4 The prep and instrumentation technicians maintain the internal Chain of Custody (COC). When the original client sample container is taken by a prep technician from the sample storage area, he/she logs the sample out as normal. Because gamma spec is a non-destructive test, samples that are designated for other tests may be used. Check with Group Supervisors if there are questions concerning sample availability or if samples are turn-around-time sensitive.

The prep technician is responsible for creating a gamma fraction on the chain of custody. The prep analyst logs out the gamma container on behalf of the counting room analyst and relinquishes the sample along with the benchsheet. After counting, the gamma spec analyst will return the samples to the sample storage area and check them in on the COC. If the aliquot taken for gamma spec is needed for other analyses, log in/log out activities are recorded on the chain of custody.

4.5 The standard filter geometry is a 47mm diameter filter mounted in a 2" stainless steel planchet. For Ra-226 analysis of a solid/soil sample, the packing must be done in a can as a GEO 17. Usually the can packing will be done on an "As Received" basis, and the % moisture data will be provided to report on a dry weight basis. If the sample volume is limited, regular Gamma can be packed as a GEO 11 and the "Ra-can" could be packed with the available sample. If the can is not filled to the top, the technician should mark a line on the outside of the container indicating the height of the actual sample and write a Quality Assurance Summary Sheet (QASS), Form 302. This documentation will help the counting analyst write a narrative about the unusual situation.

4.6 Filter samples can be digested using SOP 773 or SOP 767, then the digestate is diluted to 1000mL with DI water and packed for Gamma as GEO 1. Samples like vegetation, debris, gloves, wipes, iron bar, lead blocks, ashes, fruits, fish, cloth, wood chips etc., will be treated with different methods based on the nature of the

samples and conditions. The samples may be leached using different acids or digested and packed with different GEO. However, all geometry preparations will be documented on a QASS and a copy will be attached to the benchsheet.

5. REAGENTS AND APPARATUS

5.1 Deionized (DI) water, obtained from the laboratory's DI water system

5.2 Balance, top loading, 0.01g sensitivity

5.3 Scoops, spatulas, and tongue depressors

5.4 Graduated cylinders, 1L, type TD (to deliver)

5.5 Marinelli beakers, 2L Ga-ma # 138G, with lids, or equivalent*

5.6 Lerner Jars, 16oz., plastic, with 89mm screw lid *

5.7 Large glass/plastic funnel

5.8 Vinyl tape

5.9 Parafilm

5.10 Qualitative filter, VWR brand 313 fluted filter paper or equivalent

5.11 Cans for Geo 17, House of Cans #3104 or equivalent*

* ***Equivalent containers require approval by the Instrumentation Laboratory Supervisor.***

6. PROCEDURE

6.1 PROCEDURE FOR WATER SAMPLES

6.1.1 Samples must be properly preserved before aliquotting. Verify that the pH is less than 2, per SOP 733. If the sample contains visible sediment or other conditions exist that make preservation impractical, notify the Project Manager (PM) of the lab's intent to proceed with the unpreserved sample and document the situation on a Quality Assurance Summary Sheet.

6.1.2 Do not prepare water samples in the same workspace where soil samples are being prepared. This avoids cross contamination by dust.

6.1.3 If the sample contains sediment or suspended solids, check the work order for specific instructions as to whether or not the sample should be filtered. If it is not specified, filter per SOP 721. If the project instructions specify "Dissolved" or "Filtered", filter the sample through a fluted filter into a clean 1L graduated cylinder. Pre-filtering may be required for especially turbid samples. If the project instructions specify "Total" or "As Received," shake the sample

container to mix thoroughly and aliquot as received.

6.1.4 Liquid samples are prepared in 2L Marinelli beakers. Measure the appropriate volume of water sample in a clean 1L type TD graduated cylinder to the nearest 0.01L (i.e., 10mL). Empty the sample into a clean, labeled Marinelli beaker.

6.1.5 The gravimetric method is adapted for liquid samples other than water. Place an empty Marinelli beaker on the top loading balance and tare the balance to zero. Add the sample slowly into the Marinelli beaker until the final weight is 1000 ± 0.01g.

NOTE: If the sample volume provided falls short of the desired geometry, dilute to the appropriate geometry with DI water (e.g., dilute 600mL to 1L). *Make sure to record the original volume on the container and on the benchsheet.*

6.1.6 A method blank is made by adding a representative volume of DI water to an empty, labeled Marinelli beaker. The aliquot size used for the blank is the average volume of the sample volumes involved in the batch. The collection date for the blank is the date the samples are packed.

6.1.7 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size. For waters, indicate the following:

GEO NUMBER	LCS ALIQ.SIZE
1	1.0L

6.1.8 Attach the lid of the Marinelli beaker and seal the lid using vinyl tape. Wipe the exterior of the container with a damp paper towel to remove potential contamination. Make sure the container is labeled with the sample ID, aliquot size, date of prep and initials.

6.1.9 Submit the prepared samples to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the gamma spec analyst will check the sample back in to the storage area and fill out the internal COC.

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6.2 PROCEDURE FOR SOIL AND SLUDGE SAMPLES

6.2.1 Unless approval to the contrary is given, all soil samples must be dried and sieved through a number 4 sieve prior to preparation for gamma spec analysis. Consult SOP 721 for drying and sieving procedures.

Containers for gamma spec soils are usually prepared when the soil is being prepared for other analyses under SOP 721. The gamma spec prep worksheet for soils should be filled out manually by the prep technician at the time of packing gamma, and the electronic benchsheet will be created later on. The prep worksheet will be attached to the benchsheet when the sample is relinquished to the counting room.

The benchsheet provides information about the prep date, technician, balance number, report basis, etc., as well as all the information about how the sample was packed. Any unusual situation will be documented on a QASS (Form 302).

6.2.2 When using Lermer jars, fill the container to the appropriate level according to the desired geometry. If enough sample is provided, use Geometry 13 (500g). If not, reduce the sample volume to Geometry 11 (100g).

6.2.2.1 Sample volumes should be maintained to within ½ cm of the correct geometry height in the container.

6.2.2.2 Zero out the container weight on the balance prior to weighing out a sample.

6.2.2.3 Soil samples should be well settled into their containers by gentle shaking with the lid on. Do not pack or compress soils into the containers.

6.2.2.4 Consult the Radiochemistry Manager or Group Supervisor if the sample volume provided is less than a Geometry 11. The analysis will usually still be conducted, but the Project Manager will need to be informed because of the effects on the efficiency calibration and detection limits.

6.2.3 For Ra-226 analysis by gamma spec, the samples will be packed as a GEO 17. Generally, the samples will be packed on a "Dry" basis, however, due to rush turn around times, the sample can be packed "As Received". To accomplish this, transfer the sample to an aluminum can (appropriate for GEO 17), until it is filled to the top. Tap the can to remove air pockets and to settle the sample. Do not press or "pack" the

sample into the can. Add more sample to fill the can to the top. To ensure a tight seal, place a piece of Parafilm over the top of the can then cap the can with the metal lid and seal with the can sealer. Remove any excess Parafilm from the outside of the can.

6.2.4 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size as follows:

GEO NUMBER	LCS ALIQ.SIZE
11	100g
13	500g
17	215g
26	215g
7	1s
8	1s

6.2.5 After the preparation worksheet and the benchsheet are completed, fill out the tracking sheet and attach a copy of the work order(s) to the benchsheet. Submit the packet for a peer review.

6.2.6 Submit the samples prepared as above to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the instrument analyst will check the sample back in to the storage area and fill out the internal COC.

6.2.7 Update the status sheet with a "c" indicating that the prep is complete.

6.3 CALCULATIONS

TPU FACTORS. As defined in SOP 743, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU).

6.3.1 Water samples require a preparation uncertainty factor of 0.0504 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one volumetric measurement. See the following equation:

$$0.0504 = \sqrt{0.05^2 + 0.006^2}$$

6.3.2 Solid samples require a preparation uncertainty factor of 0.0501 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one mass measurement. See the following equation:

$$0.0501 = \sqrt{0.05^2 + 0.003^2}$$

6.3.3 In practice, these two TPU factors are substantially equivalent. To simplify the data reporting procedure, the greater of the two (0.0504) may be used for both matrices.

7. QUALITY ASSURANCE

7.1 Method blanks will be run at a frequency of five-percent (i.e., one per 20 field samples) with a minimum of one per batch. Method blanks for water consist of deionized (DI) water. Method blanks for solid samples consist of an empty container, appropriate for the geometry (i.e., 13, 11, 17).

7.2 Laboratory Control Samples (LCS) will be run at a frequency of five-percent with a minimum of one per batch. The LCS consists of a pre-made source from an outside vendor.

7.3 Duplicate samples will be run at a frequency of ten-percent with a minimum of one per batch. If insufficient volume is available for a duplicate, a count duplicate may be used.

8. SAFETY, HAZARDS AND WASTE DISPOSAL

8.1 SAFETY AND HAZARDS

8.1.1 Read the MSDSs prior to preparing standards or using any solvents or reagents for the first time.

8.1.2 Wear gloves, safety glasses, and a lab coat when working with any chemical materials (e.g., standards, solvents, reagents, or samples) or when handling materials or equipment potentially contaminated with chemicals.

8.1.3 Soil samples should be handled in a hood as much as possible to avoid inhalation and cross contamination with dust. Workspaces should be wiped down with damp paper towels whenever dust is evident and always at the end of the shift.

8.1.4 Any non-original containers that are used to hold reagents (e.g., wash bottles or automatic dispenser bottles), shall be labeled at minimum with: 1) the compound name, 2) NFPA Health, Flammability, and

Reactivity ratings, and 3) date.

8.2 WASTE DISPOSAL

8.2.1 All waste materials (e.g., filter papers, paper towels, etc.) shall be surveyed for radioactivity and disposed of accordingly.

8.2.2 All empty solvent bottles are disposed of according to the appropriate SOPs. Please note that all labels and markings must be defaced prior to disposal.

9. REFERENCES

SOP 743, "Estimating Total Propagated Uncertainties for Radiometric Analyses."

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PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 704 REVISION 7

TITLE: **ANALYSIS OF TRITIUM AND OTHER BETA-EMITTING NUCLIDES BY LIQUID SCINTILLATION COUNTING -- METHOD EPA 906.0**

FORMS: **NONE**

APPROVED BY:

TECHNICAL MANAGER _____ DATE 12/14/04

QUALITY ASSURANCE MANAGER _____ DATE 12/14/04

LABORATORY MANAGER _____ DATE 12-15-04

HISTORY: Rev0, 9/18/92; Rev1, 3/8/93; Rev2, 5/10/93; Rev3, 7/27/93; Rev4, PCN #148, 3/2/94; Rev5, 10/8/99; Reviewed and distributed without revision, 3/14/02; Rev6, 4/7/03; Rev7, 12/13/04.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform analysis of samples of various media using Paragon's two Beckman (LS6000 and LS6500) liquid scintillation counters (LSCs). These counters are each capable of sequentially and automatically acquiring data from more than 300 samples. Samples will normally be liquids in a 20mL scintillation vial, which may represent the sample directly (water samples) or indirectly (extracts from soil samples).

This procedure provides the analysis portions of EPA Method 906.0. This procedure is applicable to the determination of tritium, as well as ^{14}C, ^{63}Ni, ^{99}Tc, ^{241}Pu, ^{210}Pb, ^{147}Pm, ^{55}Fe and other beta-emitting nuclides.

Paragon also utilizes one Wallec LSC. Operation of the Wallec instrument is found in Paragon SOP 784.

2. SUMMARY

Beta emissions are detected by a fluor (i.e., a fluorescing molecule) mixed with the sample in a 20mL liquid scintillation vial, which in turn emits light in direct proportion to the beta emission energy and intensity. This light pulse is converted to an electronic pulse and recorded as a beta emission event on the instrument's multi-channel analyzer (MCA). The data collected by the MCA are subsequently interpreted by a software program, generating results in units of radioactivity per unit sample volume.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret acceptable results utilizing these methods. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or

the successful completion of an unknown proficiency test sample.

3.3 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the workorder file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. APPARATUS AND MATERIALS

This procedure is conducted with the use of installed beta detection and analysis equipment, consisting of a liquid scintillation counter (LSC), analysis software, and associated nuclear electronics and cabling. In the case of the LS6000, the data may be transferred directly to a floppy disk using a PC with the appropriate interface hardware and software. The LS6500 has these features built-in and can write to a floppy disk with an internal disk drive.

5. REAGENTS

None.

6. SAMPLE COLLECTION, PRESERVATION, HANDLING AND HOLDING TIMES

Chemical preparation steps performed for this analysis are detailed in Paragon SOPs 700, 754, 737, 799, 755, 748, 758, 726 and 772. Samples to be analyzed by this procedure will have been prepared by radiochemical procedures that include distillation of liquids, or azeotropic distillation of soils/solids.

7. PROCEDURE

7.1 OPERATING CONDITIONS

The liquid scintillation counter shall be operated according to the instructions provided by the manufacturer. All instrument settings shall be as determined during instrument installation and/or calibration. The operating conditions shall be verified daily by performance of the daily quality control checks (discussed subsequently in this SOP).

7.2 SAMPLE LOADING

Be sure the samples have been allowed to dark-adapt for a period of at least 3 hours. Normally, the samples will be placed in the rack in the order they are listed on the benchsheet. Place the rack(s) in the counter with the front (side with rack number and/or user number) facing away from the operator. The first rack to be counted must have a user number (see below for a description of user number) installed in the left (looking at the front of the rack) card slot. Subsequent racks will not have a user number card unless a different analysis is required for that rack. Ensure that the counting position of each sample is correctly recorded on

the liquid scintillation benchsheet and that the user number has the correct settings.

7.3 USER NUMBERS

User numbers provide the count and data output parameters. User number programs can be set by pressing the "Main Menu" button, then using the cursor arrows to highlight "Review and Edit User Programs". Using the cursor arrows, highlight the user number to be edited, then highlight the parameter to be set, and follow any prompts given at the bottom of the screen. For more details on setting the user number parameters, see the instrument's operating manual.

Default settings for all of the user numbers are:

- Count Blank: NO
- Two Phase: NO
- Scintillator: LIQUID
- Low Level: YES
- H#: YES
- IC#: NO
- LUMEX: YES (This option is available only on the LS6000. The LS6500 doesn't correct for luminescence.)
- Half Life Correction Date: NONE
- Sample Repeats: 1
- Cycle Repeats: 1
- Cycle Repeats: 1
- Low Sample Reject: 0
- Printer: STD
- RS232: STD

Other parameters may vary for each user number. These are:

- Manual Window Settings: In order to determine the manual window settings, a source and blank are counted on the instrument. The user number is set with Window 1 at WIDE, and the raw data output is set for Spectral Data, to give a channel by channel output. Once the data are collected, a figure of merit (FOM) is calculated to optimize the windows in order to minimize the MDC (minimum detectable concentration). Windows are set for each analysis type (i.e., ^{3}H, ^{14}C, etc.), and for each geometry type (i.e., 10mL or 5mL).
- Count Time: This depends on the required MDC and sample volume.

- Counting Precision: The instrument can be set to stop counting once a required numbers of counts have been accumulated.

7.4 DATA COLLECTION

7.4.1 **The following procedure is for the LS6000 only.** To use this option, the user number used to count the samples must have the STD RS232 Format selected.

- From the Main Menu of the support computer for the LS6000, choose "Tritium Data Capture" and press <Enter>. When the Data Capture software starts, choose "1. LS6000" <Enter>, then "1. RECEIVE data from instrument" <Enter>.

  The program will provide a table with the header "Drive and Subdirectory"; press <Enter>. Send the data to the b:\ drive (be sure that a disk is inserted into the b drive). The upper left corner of the display will read "Awaiting Response".

- Press the "Main Menu" key on the front panel of the counter. Use the cursor arrows to highlight "Automatic Counting", then press "Start" to begin counting.

  The counter will analyze each sample and generate results in CPM for each vial counted. The Data Capture software will have a message in the upper left corner which reads: "Status: Receiving Record XXXX", where XXXX is the number of the data record which will increase as samples are analyzed. The Data Capture software will now also display the filename in which the data is stored in the center of the screen. This file is named "\TRITIUM\UNXX-YYY.BSF", where XX is the user number, YYY is the next sequential number for files created with that user number, and .BSF is the default extension for Beckman Standard Format files. *Note this file name in the filename section of the benchsheet.*

- When the count is complete (i.e., LS6000 Main Menu has returned to the display), complete the liquid scintillation run log.

  To process the data, press <Esc> on the LS6000 support computer. The Status message in the upper left corner of the display, will read "Capture Completed". Press <Esc> twice to return to the Data Capture software main menu. Remove the disk from the b:\ drive and take the disk to the tritium reporting PC.

  Copy the correct file to the c:\ drive of the reporting PC. Open the "dc" program on the c:\ drive by typing "dc" then <Enter>. Use the cursor arrows to move the highlight bar to "DATA CAPTURE SUPPORT", press <Enter> to choose

this option, then choose "3. Convert BSF to dBASE File", then press <Enter>. Press 1 (Convert); the software will then prompt for "Input Filename (.BSF)" and "Output Filename (.DBF)". Type the name of the file recorded on the benchsheet, without an extension (for example, "UN01-001"), and press <Enter> for each prompt. The software will then present a default format titled "Tritium"; press <Enter> to accept this format.

A message at the bottom of the screen will read "Use actual dBase file structure (Y/N) [Y]"; press <Enter> to accept the default "Y". Then data will then be converted and displayed on the screen, with the message "Conversion Completed !".

Press <Esc> 4 times to return to the PC's Main Menu. Copy the new file to the r:\tritium directory. The data may now be accessed from any PC that is a part of the Paragon network.

7.4.2 **The following procedure is for the LS6500 only.**

- To start the sample count, press the "Main Menu" key on the front panel of the counter. Use the cursor arrows to highlight "Automatic Counting", then press "Start" to begin counting. The counter will analyze each sample and generate results in CPM for each vial counted.

- When the count is complete (LS6500 Main Menu has returned to the display), complete the liquid scintillation run log.

- To create a disk to transfer run information from the LSC to the tritium reporting PC, select "Data Management" from the main menu on the LS6500. Next select "Access Data Buffer/Disk", then select "Move Files to Disk". Enter the user number for the files that you want to move.

7.5 SAMPLE ANALYSIS (FROM EITHER THE LS6000 OR LS6500)

- Move the desired .ASC file into "I:\Operations\LSC\LIMS Data." When the file is moved, add the letter "Y" in front of the file name to denote that the file is from instrument LS6500 or add the letter "X" in front of the file name to denote that the file is from instrument LS6000. The file can be opened in Excel and reviewed to ensure that the correct file has been chosen. *CAUTION - when exiting Excel, be sure that the file is not saved in the incorrect format.*

- The tritium data is analyzed using the LIMS (Laboratory Information Management System). Open the LIMS program and create an analytical run by selecting "Laboratory" and "Analytical Run Entry"

from the main menu. Analytical runs are typically named by adding a letter to the prep batch ID. For example, the analytical run created from prep batch 3H051204-2 would be 3H051204-2a.

For the analytical run, the instrument ID is 'LIQSCINT', the analytical department is 'LS,' and the analysis method is 'PAI 704'. *Note there are several PAI 704s listed (i.e., PAI 704_Tc99).*

- Enter the "RackNum" and "PosNum." These are the rack and position numbers. Go to the "Radiochemistry Data Import Menu" page. Enter the file name (i.e., YU0573102) and the analysis method, and click 'Import Data Files'.

  After the data is imported, select 'Review Import Results'. This is the location where the background values are entered (in the BkgCPM column) and efficiency values (in the EffBase column).

- The efficiency will be entered as a decimal (i.e., enter 0.347 for an efficiency of 34.7%). Next select "Move Data Files to Holding Area", followed by "Merge Analytical Run".

- Return to the "Analytical Run Information" page. Select "Validate Run". After the run is validated, return to the "Radiochemistry Data Import Menu".

- Select "Process Preliminary Results", followed by "Merge Analytical Data". Return to the main menu and select "Reporting" and "Results – Reporting". Enter the Analytical Run ID, the Prep Batch ID, the QC Batch ID, and the QC Order Number.

  Select "Manage Data Packages" and "Create/Add" to create the data package. You may print out a Raw Data Results Summary page by selecting "Radchem/Summary Review" and "Generate Reports". This print out should be checked for accuracy. *If the data was manually entered, every data point needs to be checked.*

7.6 CALIBRATION PROCEDURES

7.6.1 Efficiency Calibration Standards for calibration shall be traceable to the National Institute for Standards and Technology (NIST). Standards for tritium counting will normally be prepared from commercially available NIST-traceable stock solutions. The analysis system shall be calibrated at least annually.

- Three blanks of the same geometry are prepared with DI water and cocktail, and are used for background correction.

- A one-point efficiency is highly accurate and will be used for the calculation of all results showing the Quench Indicating

Parameter result corresponding to the average observed for the calibration standard (within ±10 % relative efficiency or lacking this calibrated range, ±15 of mean H-numbers). Any sample falling outside this range will be calibrated by sample specific addition of a minimum known volume (<200 µL) of NIST-traceable standard. The efficiency from sample specific standard additions is calculated as defined below:

$$\text{Deteff} = \frac{(\text{SSGrCPM} - \text{SmplGrCPM})}{\text{SpkDpm}}$$

In some instances, it may be necessary to prepare a quench curve to establish a relationship between the counting efficiency and the Quench Indicating Parameter (H#). In general, the standards will be prepared by spiking each with a known concentration of the standard and the same volume of cocktail. A quenching agent, such as nitromethane, will be added in increasing increments. The sample specific efficiency will be determined as a function of the H#.

7.5.1 Background calibration (reagent blank) An aliquot of DI water equivalent to the calibration geometry is transferred to a scintillation vial independent of the preparation process and cocktail added such that the calibration geometry is recreated. One reagent blank is submitted for each preparation batch and counted for a time period equal to or greater than the longest sample count. For samples counted in the default calibration geometry (i.e., 10mL water + 10mL cocktail), CPM results (as well as blank ID and count time) of the reagent blank count are entered into a spreadsheet (see below for location of spreadsheets), which tracks the running mean of the last seven reagent blanks, and compares each blank to historical control limits established from the first 30 data points in the population (±3 sigma).

The current running mean of the reagent blank CPM is used as the background in the calculation of associated results for the associated preparation batch. For other beta-emitting analyses which are performed infrequently or for which the "running mean background" mentioned above would not be appropriate, a Reagent Blank should be counted with each batch. The result of the Reagent Blank count will be used as the instrument background for reporting purposes.

Reagent blank spreadsheets are located at R:\inst\lsc\ls6500 or ls6000\prg\: rb_c14.xls, rb_fe55.xls, rb_h3.xls, rb_ni63.xls, rb_tc99.xls, rb_tota.xls, rb_h3_5.xls, and rb_p241.xls.

8. QC MONITORING

8.1 GENERAL

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the laboratory's internally derived acceptance criteria.

8.2 DAILY QA CHECKS

Standards for Daily QA Checks consist of unquenched ^{3}H and ^{14}C standards (NIST-traceable), a flame-sealed, vendor-supplied background, and an in-house prepared blank sample.

8.2.1 Place the unquenched ^{3}H calibration standard in position 1, the unquenched ^{14}C calibration standard in position 2, the blank in position 3, and the vendor-supplied background in position 4 of the sample rack labeled "User No. 1", and place the rack in the right front position in the counter. Place the "HALT" (red) rack immediately after the "User No. 1" rack.

8.2.2 Start the Daily checks by pressing "Main Menu", selecting "Automatic Counting" from the menu with the cursor arrows, then pressing "Start" to begin the counting sequence. The QA Check process will initiate a 10 minute count of the ^{3}H standard, the ^{14}C calibration standard, the blank, and the vendor-supplied background. At least 100,000 counts should be acquired for the ^{3}H and ^{14}C check sources.

8.2.3 When the count is complete, enter the count results for the standards and blank in the LSQA spreadsheet (located at R:\inst\ls6000\prg\ lsqa6000.xls or R:\inst\ls6500\prg\lsqa6500.xls) using a network computer. Count results from Window 1 are used for the ^{3}H standard, count results from Window 2 are used for the ^{14}C standard, and count results from Window 1 are used for the blank and vendor-supplied background.

The spreadsheet compares each count result to historical control limits established from the first 30 data points in the population. Control limits are set at ±3 standard deviations (above and below) the means for the standards and blank. If any of the current data points fall outside the default control limits of ±10% of the mean, re-analyze the QC samples. If the current data points are still outside of control limits, do not operate the instrument until notifying the Supervisor and resolving the problem. *Note that Paragon does not control on the results of the flame sealed vendor-supplied background sample.*

9. CALCULATIONS AND INTERPRETATION OF DATA

9.1 DATA CALCULATIONS

The liquid scintillation instrument calculates sample counts per minute (CPM) for each sample. This "raw" data is provided to an analysis computer, either by

manual entry or by transfer via RS-232 serial protocol. Both data transfer methods provide the user with several full-screen, editable sample information pages to be used for verification of sample and counting data. The "raw" data provided to the analysis and reporting program is modified in several ways to generate final results, as described below.

9.1.1 Sample Result or Activity (A), reported as activity/unit mass or volume.

$$A = \frac{SampleCPM - BlankCPM}{VCEe^{-\lambda t}}$$

where:

V = the sample volume; normally 0.01L

C = the conversion from count rate to activity units; normally 2.22 DPM/pCi. If sample result is desired in Bq, this factor is 1/60 (1 Bq is 1 disintegration per second (DPS))

E = the fractional counting efficiency

$e^{(-\lambda t)}$ = the decay correction from sampling to counting

9.1.2 The counting uncertainty (CU) is reported in units of activity per mass or volume. It is determined for the 1σ level of uncertainty.

$$CU = K\sqrt{SampleCPM \cdot T + BlankCPM \cdot T}$$

where:

T = the time elapsed during sample counting

K = $1/(VTCE\ e^{(-\lambda t)})$

Total Propagated Uncertainty (TPU)at the one sigma level

$$TPU = \sqrt{CU^2 + (IU * A)^2 + (PU * A)^2}$$

where:

A = the sample activity or result

IU = 0.056

PU = the uncertainty propagated by sample preparation (see Test specific Paragon SOPs)

9.1.3 Sample specific Minimum Detectable Concentration (MDC)

$$MDC = K \cdot (2.71 + 4.65 \cdot S_b)$$

where:

K = 1/(VTCE e(-λt))

V = the sample volume

T = the counting time for the background count

C = the conversion from count rate to activity units

E = the fractional counting efficiency

e(-λt) = the decay correction from sampling to counting

Sb = (T*BKG Count Rate)$^{1/2}$

This MDC equation is fundamentally the same as those offered in references (12.3) to (12.4), which represent industry standard methodology for analyses of these types.

9.1.4 Decision Level (DL)

$$DL = 2.33 \cdot S_b \cdot K$$

where:

K = 1/(VTCE e(-λt))

V = the sample volume

T = the counting time for the background count

C = the conversion from count rate to activity units

E = the fractional counting efficiency

e(-λt) = the decay correction from sampling to counting

Sb = (T*BKG Count Rate)$^{1/2}$

9.1.5 The analysis results, along with all of the related sample information, is written to a comprehensive database of analyzed tritium samples. When all of the sample data has been entered into the program and the operator discontinues data entry, the database is searched for all new data entries from the current session. New data is sorted by client for reporting. The reporting software then generates individual reports by client as requested by the operator.

9.2 INTERPRETATION OF DATA

9.2.1 Analysis results should be spot-checked on a monthly basis, with one sample being checked manually for accurate calculation of the result or MDC by the reporting software. This may be aided by the use of a spreadsheet with the appropriate equations, provided the spreadsheet has been validated by the QC Officer. (See SOP 315). The results of the manual calculation should be filed by the analyst for subsequent auditing purposes.

9.2.2 Analysis results should be checked for consistency between results of duplicates, blanks, and spiked samples, and the MDC results should be checked to confirm that the client's required MDC is met. All results must be reviewed according to PAI SOP 715, Review of Radioanalysis Data.

10. DEVIATIONS FROM METHOD

This procedure contains no known deviations from EPA 906.0.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

11.1.1 Normal laboratory safety procedures must be complied with during the conduct of this procedure. No special safety requirements are mandated by this procedure.

11.1.2 High voltage in the range of 1000 volts DC is applied to the photomultiplier tubes in these instruments. This can result in electric shock if the instrument is disassembled with power applied. To minimize the possibility of electric shock, turn off the power and unplug the instrument prior to any disassembly.

11.2 WASTE DISPOSAL

Liquid scintillators contain a solvent and an emulsifying agent to promote mixing with aqueous samples. The solvents used by Paragon are biodegradable, but may not be suitable for sewer disposal. Additionally, the samples may contain concentrations of radioactivity above sewer disposal limits. Contact the Waste Disposal Coordinator and/or Radiological Safety Officer (RSO) for disposal instructions.

12. REFERENCES

12.1 Beckman LS6000 Series Liquid Scintillation System Operators Manual, June 1991.

12.2 Beckman LS6500 Series Liquid Scintillation System Operators Manual.

12.3 Lloyd A. Currie, "Limits for Qualitative Detection and Quantitative Determination", Analytical Chemistry, Volume 40, pages 586-593, March 1968.

12.4 National Council on Radiation Protection and Measurements (NCRP), Report No. 58, page 309, September 1984.

12.5 EPA 520/1-80-012, "Upgrading Environmental Radiation Data", Health Physics Society Committee Report HPSR-1, pages 6-26, August 1980.

TABLE 1

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency, Background and Quench Factor Checks	Daily	Within derived control limits.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Efficiency Calibration	Yearly	For single point efficiency calibrations, the value must be within ±5% of the previous calibration value. For quench curves, the fitted values shall be within ±5% of the observed value for each point on the curve. Post-calibration method spikes (LSCs) shall meet normal LCS acceptance criteria.	Tag method off-line. Determine and correct problem; verify source activity, recount and/or recalibrate or document why condition is acceptable.
Background Calibration	Continuous	Control limits set from initial calibration run.	Tag method off-line. Determine and correct problem, re-establish limits; or document why condition is acceptable.
Chemical Yield	Each sample, where method allows	Each sample meets current control limits for analysis.	Re-prep; or qualify or narrate why condition is acceptable.
Spectral Interferences	Evaluate each result for spectral interferences	WIND2 count rate within current control limits or interfering activity does not compromise quantitation	Re-prep/recount affected samples; consult with Supervisor or Department Manager; determine and correct problem; or qualify or narrate why condition is acceptable.

NOTE: This SOP and SOP 715 contain acceptance criteria and corrective actions for method blank, laboratory control samples (LCSs), duplicate samples and matrix spike/matrix spike duplicates (MS/MSDs).

PARAGON ANALYTICS
STANDARD OPERATING PROCEDURE 726 REVISION 4

TITLE: **DETERMINATION OF LEAD-210 IN SOILS, SEDIMENTS, AND WATERS**

FORMS: **302**

APPROVALS:
TECHNICAL MANAGER _____ DATE 12/15/04
QUALITY ASSURANCE MANAGER _____ DATE 12/15/04
LABORATORY MANAGER _____ DATE 12-15-04

HISTORY: Rev0, 11/16/93; Rev1, 5/3/96; Rev2, 4/26/02; Rev3, 4/4/03; Rev4, 12/15/04.

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary for preparation of environmental soils, sediments, and waters for quantitative measurement of ^{210}Pb.

2. SUMMARY

2.1 Pb in soils and sediments is solubilized using nitric, hydrofluoric and hydrochloric acids.

2.2 Pb is pre-concentrated by passing the sample through a cation exchange column. A chromatographic resin with a high affinity for Pb is used to isolate ^{210}Pb from potentially interfering radionuclides. In nitric acid, Pb is retained on the resin while other unwanted sample constituents are not. Pb is stripped from the resin with hydrochloric acid. The purified solution containing Pb is mixed with liquid scintillation cocktail and counted in a liquid scintillation counter (LSC instrument). Stable Pb, added into the samples at the beginning of the procedure to monitor the chemical recovery, is measured in the sample by ICP AES before and after chemical separation.

2.3 Air filters may be analyzed by using the soil procedure.

2.4 This procedure may also be used for suspended solids deposited on filters. The dried filter may enter the procedure directly at the grinding stage of sample preparation. The sample aliquot weight, in this case, will have to be adjusted to account for the weight of the filter. The adjusted weight should be calculated on a Quality Assurance Summary Sheet (QASS, Form 302) and recorded on the benchsheet as the sample weight. The remainder of the preparation procedure is identical to that for a soil sample.

2.5 The resin also retains Sr, and with some slight modifications, this method can be utilized for a sequential preparation of both Pb and Sr. Pb and Sr are both loaded onto the column in nitric acid. Sr is stripped from the column in dilute nitric acid while Pb is retained. Once the Sr has been removed, Pb is stripped from the column with HCl. Refer to SOP 707 for the preparation of Sr samples.

2.6 Actinides are not retained on the resin, and will pass through when Pb and Sr are loaded onto the column. Therefore, the column effluent from the load solution and subsequent rinses can be collected and saved for use in actinide separation and purification methods.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file information indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

This SOP is applicable to water and soil samples that do not contain significant concentrations of organically complexed Pb. Organically complexed Pb may not be retained by the cation exchange column. Consequently, samples that are suspected to contain organically complexed Pb should be muffled at 450°C for at least one hour.

5. APPARATUS AND MATERIALS

5.1 Disposable ion exchange columns: 15mL resin volume with attachable funnel to receive 2L bottle (Environmental Express part nos. R1010 and R1030).

5.2 Cation exchange column: Precondition a disposable plastic column with 2-3mL of methanol (the frit at the orifice of the column is hydrophobic). Transfer AG50x8 (or AG50x4) resin to the stem of the column as a slurry with DI water to the 7cm mark. Attach the funnel to the column (make certain that the column and funnel fit tightly).

5.3 Sr Resin™ column: Use a Bio-Rad column (catalog #731-1553) or equivalent and transfer the Sr Resin to the column as a slurry with water. Add resin up to approximately the 1.6mL mark on the column. The Sr Resin is held in place by a layer of clean silica sand on top of the resin bed.

5.4 Eppendorf pipets, or equivalent

5.5 Pipet tips

5.6 Graduated cylinder, 1L

5.7 Disposable plastic bottles, 2L

5.8 Polypropylene beakers with lids, 250mL (8 oz)

5.9 Polypropylene beakers with lids, 100mL

5.10 Balance with 0.01g resolution

5.11 Test tubes, disposable, 15mL

5.12 Plastic graduated cylinder, 25mL

5.13 Disposable glass cups

5.14 Liquid scintillation vials

5.15 Transfer pipets, 7mL polyethylene disposable (VWR Cat. No. 14670-103 or equivalent)

5.16 Parafilm

5.17 Hot Block (Environmental Express or equivalent)

5.18 Steam bath

5.19 Vortex mixer

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is not hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 NIST-traceable ^{210}Pb spiking solution.

6.2 Pb carrier, 1.0 mg Pb/mL: Dissolve 1.60g Pb $(NO_3)_2$ in 1000mL of DI water. TLV = 0.05mg/m^3 = 0.006 ppm (TWA).
The Pb carrier reagent must be analyzed by ICP to accurately determine the Pb concentration. This is accomplished by diluting the Pb carrier reagent 1000-fold with ICP diluting solution. Prepare in triplicate and submit to the Metals Lab for

analysis. The preparation and standardization of this reagent must be documented in the Reagent Preparation Logbook.

6.3 Nitric acid 16N, concentrated, reagent grade. TLV = 2ppm (TWA). Irritant, corrosive.

6.4 Hydrofluoric acid, 48% reagent grade. TLV = 3 ppm.

6.5 Hydrochloric acid 12N, reagent grade. TLV = 5 ppm (ceiling). Irritant, corrosive.

6.6 Nitric acid, 8N : Cautiously add 500mL of conc. HNO_3 to approximately 400mL of DI water and dilute to 1 L. See 6.3 for TLV.

6.7 Nitric acid, 0.1N: Add 6.3mL conc. HNO_3 to approximately 900mL DI water and dilute to 1L. See 6.3 for TLV.

6.8 Nitric acid, 0.05N: Add 3.1mL conc. HNO_3 to approximately 900mL DI water and dilute to 1 L. See 6.3 for TLV.

6.9 Nitric acid, 1N: Add 63mL conc. HNO_3 to approximately 900mL DI water and dilute to 1L. See 6.3 for TLV.

6.10 Hydrochloric acid, 6N: Add 500mL of conc. HCL to 400mL of DI water and dilute to 1 L. See 6.5 for TLV.

6.11 Hydrochloric acid, 4N: Cautiously add 330mL conc. HCl to 500mL DI water and dilute to 1L. See 6.5 for TLV.

6.12 Hydrogen Peroxide, ACS grade, 30%. TLV = 1 ppm (TWA).

6.13 ICP diluting solution: Carefully add 10mL of conc. nitric acid and 50mL of hydrochloric acid to 940mL of DI water. See 6.3 and 6.5 for TLVs.

6.14 Cation exchange resin, AG50x8 or AG50x4.

6.15 Sr Resin™ chromatographic resin (particle size 50 - 100 µm). Purchased from Eichrom Industries, Inc. (Darien, IL).

6.16 Radiacwash®.

6.17 Methanol, reagent grade. TLV = 200 ppm (TWA).

6.18 Ultima Gold LLT™ liquid scintillation cocktail.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 per liter of sample to bring the pH to 2 (15mL of 1N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without

preservation, they should be brought to the laboratory within 5 days, then preserved (A), and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

7.2 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

8. PROCEDURE

8.1 SOIL PREPARATION- Soils/sediments must be prepared through the grinding stages of SOP 721.

NOTE: The acid dissolution procedure for ^{210}Pb in soil is identical to SOP 773 - Dissolution of Solids for Determination of Actinides, *except for the following*:

- Soils that require muffling will be muffled at a maximum temperature of 450°C.
- Conc. HCl is added to the sample when re-dissolving the salts at the end instead of conc. HNO_3.
- Boric acid is not added to the sample when redissolving the salts at the end.

8.1.1 Weigh 2.0g of soil (dry and finely ground) into a 250mL polypropylene beaker. Record weight (W_s) on the benchsheet.

8.1.2 Prepare a blank and blank spike per Section 9.1. If other tests are being prepared sequentially with Pb, the appropriate tracers, spikes and/or carriers should be added at this time.

8.1.3 Add 1.0mL of 1.0mg/mL Pb carrier solution.

NOTE: A replicate 1.0mL aliquot (or similar known volume from a calibrated pipettor) of Pb carrier is diluted by adding 5mL of concentrated HCl and diluting to 1L with DI water. After mixing thoroughly, a 10mL aliquot of this dilution is transferred to a test tube labeled "reference carrier" and submitted with the initial and final tubes for ICP analysis.

8.1.4 Add 25mL conc. HNO_3 to each beaker using a volumetric dispenser.

8.1.5 Using a **plastic** graduated cylinder, add 25mL conc. HF to each beaker (do not allow HF to come into contact with any type of laboratory ware made of glass since HF will dissolve glass).

8.1.6 Add 25mL of conc. HCl to each beaker. Place a 100mL polypropylene beaker as a cover onto the 250mL beaker containing the sample.

8.1.7 Allow the samples to pre-digest at least 1 hour at room temperature to allow any vigorous reaction to subside.

8.1.8 Place the beakers on the steam bath and heat for at least 4 hours.

8.1.9 Uncover the beakers and take to dryness on the steam bath.

8.1.10 For samples with low organic content, skip Section 8.1.13. For samples with significant organic content proceed to Section 8.1.11.

8.1.11 Remove from the steam bath and add 10mL conc. HNO_3. An additional 5mL 30% H_2O_2 can be added to assist with dissolution of difficult matrices. Since the addition of H_2O_2 can result in a vigorous reaction, the samples should be allowed to stand at room temperature for a few minutes. After the reaction has subsided, return the beaker to the steam bath and take to dryness.

8.1.12 Remove from the steam bath and add 10mL conc. HCL and about 140mL DI water to solubilize the solids. Mix well. Return beakers to the steam bath for about 15min. to warm solution and enhance dissolution of salts.

8.1.13 Transfer the sample through a qualitative fluted filter paper into a 1L graduated cylinder. Rinse the beaker two or three times with DI water and transfer the rinsate to the filter.

8.1.14 Dilute to a final volume (V_s) of 1L with DI water and transfer to a clean, labeled 2L plastic bottle.

8.1.15 Mix each sample thoroughly by capping and shaking. Pipet a 10mL aliquot from each sample into a disposable test tube. Cover with Parafilm and label with the sample ID and "initial Pb" (C_i).

8.1.16 Prepare a cation exchange column per Section 5.2. Attach a funnel to the column, making sure they fit tightly to avoid leaking. Condition the column with ~30 mL of 1N HNO_3.

8.1.17 Pass the sample through the column at a rate of about 1-2 mL/min. This is accomplished by inverting the 2L bottle into the funnel that is attached to the top of the cation exchange column. The sample will feed automatically through the column.

8.1.18 After the sample has completely passed through the resin, rinse the column with 10mL of 0.1N HNO_3.

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8.1.19 Discard the feed and rinse solutions into the Paragon wastewater treatment facility.

8.1.20 Elute Pb and other cations with 50mL of 8N HNO_3. Collect the solution in a labeled 250mL beaker.

8.1.21 Place on a steam bath and evaporate to dryness.

8.1.22 Extrude the resin from the column and collect in a wide mouth jar labeled "hazardous waste-used acidic resin" in the satellite accumulation area. When the satellite container is full, notify the site Waste Management Officer for further instructions. Soak the empty columns in RadiacWash®, rinse with tap water, and discard into the sanitary trash.

8.1.23 Once dry, dissolve the salts in 5mL of 8N HNO_3 solution. Add the acid to the specimen cup while the sample is still on the steam bath to facilitate complete dissolution of the salt residue.

8.1.24 Proceed to Section 8.3 of this SOP.

8.2 WATER PREPARATION

8.2.1 Using a graduated cylinder, measure the sample to the nearest graduation and transfer into a 2L disposable plastic bottle (usual sample volume = 1L). If the sample is not 1L, dilute with deionized water to 1L. Record the volume on the bench sheet (V_i).

8.2.2 Prepare a blank and blank spike per Section 9.2. If sample is to be run sequentially for other tests, the appropriate tracers, spikes and/or carriers should be added at this time.

8.2.3 Add 1.00mL of 1.0mg Pb/mL carrier (1.0mg Pb) (S).

NOTE: A replicate 1.0mL aliquot (or similar known volume from a calibrated pipettor) of Pb carrier is diluted by adding 5mL of concentrated HCl and diluting to 1L with DI water. After mixing thoroughly, a 10mL aliquot of this dilution is transferred to a test tube labeled "reference carrier" and submitted with the initial and final tubes for ICP analysis.

8.2.4 Mix sample thoroughly by inverting bottle several times and remove a 10mL aliquot (R_i) for ICP determination of Pb. Place aliquot in 15mL test tube, seal with Parafilm and label with sample I.D. and "initial-Pb" (C_i).

8.2.5 Prepare a cation exchange column per Section 5.2. Attach a funnel to the column, making sure they fit tightly to avoid leaking. Condition the

column with ~30 mL of 1N HNO_3. Pass the sample through the column at a rate of about 1-2 mL/min. This is accomplished by inverting the 2L bottle into the funnel that is attached to the top of the cation exchange column. The sample will feed automatically through the column.

8.2.6 After the sample has completely passed through the resin, rinse the column with 10mL of 0.1N HNO_3.

8.2.7 Discard the feed and rinse solutions into the Paragon wastewater treatment facility.

8.2.8 Elute Pb and other cations with 50mL of 8N HNO_3. Collect the solution in a labeled 250mL polypropylene beaker. Place on a steam bath and evaporate to dryness.

8.2.9 See section 8.1.22 above for column and resin disposal.

8.2.10 Dissolve the salts in 5mL of 8N HNO_3 solution. Add the acid to the specimen cup while the sample is still on the steam bath to facilitate complete dissolution of the salt residue.

8.2.11 Proceed to Section 8.3 of this SOP.

8.3 Pb PURIFICATION WITH Sr Resin™

8.3.1 Precondition a Sr Resin™ column (see Section 5.3 for preparation of Sr Resin™ columns) with 5mL of 8N HNO_3, collecting the rinsate in a disposable waste cup.

8.3.2 Transfer the sample solution to the column using a disposable transfer pipet.

8.3.3 Using the disposable transfer pipet, rinse the beaker with 2mL of 8N HNO_3 and add the rinsate to the column. Allow the entire sample solution to pass through the column.

8.3.4 Collect the solution that drains from the column in a disposable waste cup. Repeat this rinse as described in the previous Step two more times for a total of three rinses, allowing each rinse to pass completely through the column before adding the next.

8.3.5 The contents of the waste cup can be discarded into the Paragon wastewater treatment facility via the laboratory sink followed by plenty of cold tap water. The disposable cups may be rinsed with RadiacWash® solution and tap water and re-used for collecting waste column effluent. If the cups are not needed they may be soaked in

RadiacWash®, rinsed with tap water, and discarded into the sanitary trash.

8.3.6 Rinse the column with two 5mL aliquots of 0.05N HNO_3. Collect the solution that drains from the column in the disposable waste cup. Record the date and time to the nearest 10 minutes of the end of the last rinse on the benchsheet. This is the starting time of the ^{210}Bi ingrowth.

8.3.7 The contents of the waste cup from Step 8.3.6 should be discarded into the Pb process waste container provided by the Waste Management Officer.

8.3.8 Elute Pb from the column with 30mL of 6N HCL (V_{Pb}). Collect the eluate in a labeled disposable glass cup.

8.3.9 Add 5mL of 16N nitric acid to the eluate. This will aid in breaking down organic constituents in the column effluent.

8.3.10 Take the samples to dryness by placing the glass cups on a Hot Block set at 100°C.

8.3.11 Once dry, dissolve the residue by adding 1.0mL of 4N HCl. Cap the glass cups and vortex to mix completely. Allow to stand and vortex intermittently several times to be sure all of the Pb is in solution. Add 5.0mL of DI water. Cap and vortex again.

8.3.12 Pipet 0.1mL from the thoroughly-mixed sample and transfer to a test tube labeled with the sample ID and "final-Pb" (C_f). Dilute to 10.0mL by adding 9.9mL of ICP diluting solution. Cap the test tube and invert several times to mix thoroughly.

8.3.13 Submit the "initial" and "final" aliquots to the metals department for ICP determination of Pb for calculation of the chemical yield.

8.3.14 Upon the return of the ICP sample fractions to the lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the Paragon waste water treatment facility (down the drain in the lab sinks with plenty of cold tap water). The test tubes may be rinsed with RadiacWash® solution, followed with tap water, and discarded into the broken glass receptacle.

8.3.15 From the remaining sample in the glass cups, pipet 5.0mL into a plastic liquid scintillation vial. Add 15mL of Ultima Gold LLT™ cocktail to each vial. Cap and shake well to mix. Since the liquid scintillation vial is an optical surface, all labeling should be done on the cap, not on the vial itself. Wipe each vial down using a kimwipe moistened with methanol.

8.3.16 Relinquish the samples to the instrument lab for counting by liquid scintillation with all appropriate documentation. The LS vials will be analyzed and ultimately disposed of in the manner described in SOP 704.

8.4 PREPARATION OF CALIBRATION STANDARDS

8.4.1 Provide the counting lab with a total of twenty-four liquid scintillation vials consisting of twelve blanks and twelve LCSs with approximately 1000-2500dpm of NIST-traceable ^{210}Pb in each. The blanks and LCSs should be quenched with nitromethane in increments of 15µL.

8.4.2 To accomplish this, label twenty-four 2L disposable plastic bottles. Fill each with 1L of acidified DI water. Add 1mL of Pb carrier to each. Spike the twelve LCSs. Process like water samples, following this SOP (starting with Section 8.2.4). Once samples have been transferred to liquid scintillation vials and cocktail has been added, quench with a range of 0-165µL of nitromethane in 15µL increments for both the blanks and LCSs. Shake to mix and wipe the vials with a kimwipe moistened with methanol. Relinquish to the counting lab with appropriate documentation.

9. CALCULATIONS

The following parameters must be recorded on the benchsheet. The parameters are necessary to calculate chemical recovery and also to provide the instrumentation group with the sample aliquot size to be used in calculating the final results.

9.1 PARAMETERS

9.1.1 Soil Samples

W_s = dry weight of soil (g). Refer to Section 8.1.1.

V_s = final volume of sample (mL). Refer to Section 8.1.14.

C_i = concentration of Pb determined in "initial-Pb" aliquot (µg/mL). Refer to Section 8.1.15.

C_F = concentration of Pb in eluate (µg/mL). Refer to Section 8.3.12.

V_{Pb} = volume of eluate (mL). Refer to Section 8.3.8.

9.1.2 Water Samples

V_i = initial sample volume (mL). Refer to Section 7.2.1.

A = volume of acid added to bring sample to 0.1N acidity (mL). Refer to Section 7.1.

S = volume of Pb carrier solution spiked into sample (mL). Refer to Section 8.2.3.

R_i = volume of solution removed for "initial - Pb" ICP analysis (mL). Refer to Section 8.2.4.

C_i = concentration of Pb determined in "initial - Pb" aliquot (µg/mL). Refer to Section 8.2.4.

V_{Pb} = volume of Pb eluate (mL). Refer to Section 8.3.8.

C_F = concentration of Pb in Pb eluate (µg/mL). Refer to Section 8.3.12.

9.2 CHEMICAL RECOVERY CALCULATIONS
Calculate chemical recovery using the following calculations:

9.2.1 Soil Samples

Pb_i = initial mass of Pb (µg) = $(C_i)(V_s - 10)$

The factor of 10 accounts for the aliquot removed for ICP analysis. Refer to Section 8.1.15.

$Pb_F = (C_F)(V_{pb})(100)$

The factor of 100 accounts for the dilution made prior to ICP analysis. Refer to Section 8.3.11.

% Pb recovery = $(Pb_F / Pb_i)100$

Chemical recovery results must be submitted to instrumentation group.

9.2.2 Water Samples

Pb_i = initial mass of Pb (µg) = $(C_i)(V_i + A + S - R_i)$

Pb_F = final mass of Pb recovered (µg) = $(C_F)(V_{Pb})100$

% Pb recovery = $(Pb_F / Pb_i)(100)$

Chemical recovery results must be submitted to instrumentation group.

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9.3 SAMPLE ALIQUOT SIZE TO BE USED IN FINAL RESULTS CALCULATION

9.3.1 For soils, the sample aliquot mass to be used in calculating the final results must be reduced slightly since two aliquots were removed to determine chemical recovery. This correction is rather insignificant (approximately 2%).

W_c = sample mass used in calculation of final results (g).

$$= W_i \times [(V_s - 10) / (V_s)] \times [(10 - 0.10) / (10)]$$

9.3.2 For waters, the sample aliquot volume to be used in calculating the final results must be reduced slightly since two aliquots were removed to determine chemical recovery. If 1 L of water is used for analysis, this correction is rather insignificant (approximately 2%). The correction becomes more significant for smaller initial sample volumes.

V_c = sample volume used in calculation of final results (mL).

$$= V_i [V_i + A + S - R_i) / (V_i + A + S)]$$

9.3.3 W_c and V_c must be submitted to the instrumentation group in order to allow calculation of the final results.

9.4 ACTIVITY CALCULATION

Calculate ^{210}Pb activity in pCi/aliquot as follows:

$$= \frac{(GCPM - BCPM)}{(WcorVc) * 2.22 * ChemicalYield * Pbefficiency * decay}$$

9.5 TPU FACTORS

As defined in SOP 743, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty.

9.5.1 Water samples require a preparation uncertainty factor of 0.1033 (1σ). This is based on one gross aliquotting, two quantitative transfers, one volumetric measurement, and one ICP yield determination.

$$0.1033 = \sqrt{.05^2 + .025^2 + .025^2 + .006^2 + .083^2}$$

9.5.2 Solid samples require a preparation uncertainty factor of 0.1062 (1σ). This is based on one gross aliquotting, three quantitative transfers, one volumetric measurement, and one ICP yield determination.

$$0.1062 = \sqrt{.05^2 + .025^2 + .025^2 + .025^2 + .003^2 + .083^2}$$

9.5.3 In practice, these two TPU factors are not significantly different. To facilitate the use of the radiochemistry reporting software, the greater of the two (0.1062) may be used for both matrices.

10. QUALITY CONTROL

10.1 SOIL SAMPLES

10.1.1 One blank using 2g of quartz sand is run per batch of 20 samples, or at a 5% frequency.

10.1.2 One sample duplicate is run per 10 samples, or at a 10 % frequency.

10.1.3 One laboratory control sample (spiked quartz sand) is run for each batch of 20 samples (5% frequency) with a range of 10 to 30pCi ^{210}Pb/per gram.

10.2 WATER SAMPLES

10.2.1 One blank using 1L containing 5mL of concentrated HCl and 995mL of DI water is run per batch of 20 samples or at a 5% frequency.

10.2.2 One sample duplicate is run per 10 samples or at a 10% frequency.

10.2.3 One laboratory control sample (spiked blank, 1L, containing 5mL of concentrated HCl and 995mL of DI water) is run for each batch of 20 samples (5% frequency) with a range of 10 to 30 pCi ^{210}Pb.

11. SAFETY, HAZARDS, AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

Care should be taken when diluting acids. Always add acids to water, <u>not</u> water to acid.

11.2 WASTE DISPOSAL

11.2.1 Aqueous waste from Sections 8.1.19, 8.2.7 and 8.3.5 can be disposed down the laboratory sink drain.

11.2.2 Solutions collected in Section 8.3.7 should be placed in a waste container provided by the Waste Management Officer.

12. REFERENCES

12.1 E.P. Horwitz, R. Chiarizia, and M. Dietz, "A Novel Strontium- Selective Extraction Chromatographic Resin", Solvent Extraction and Ion Exchange, 10 (2), 313-336 (1992). Note: This reference presents data that shows the strong retention of Pb by the Sr•Spec chromatographic resin. Pb retention exceeds Sr retention by more than two orders of magnitude at certain activities.

12.2 Don Nelson, Argonne National Laboratory, Personal Communication, March 1993.